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NONLINEAR VISCOELASTICITY AND THIXOTROPY OF A SILICONE FLUID

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ABSTRACT: The nonlinear rheological properties of a silicone fluid (PDMS) sample of high viscosity are reported in this paper. Small amplitude oscillatory shear curves and steady shear flow curves of the sample are measured in the temperature range from 0 °C to 120 °C. This silicone fluid obeys the time-temperature superposition feature, which enabled to set up a 5-element Maxwell-model that accurately describes the viscoelastic properties of the silicone fluid in the linear region. However, this silicone fluid is shear thinning, the samples obey the Cox-Merz rule, and other measurements also indicate that it is a nonlinear material regarding both the viscous and the elastic properties. Multimode White-Metzner model is constructed that accurately describes the nonlinear viscous properties. Long time shear flow measurements show that these samples are thixotropic at 80 °C.
KEYWORDS: silicone fluid, PDMS, Maxwell model, nonlinear fluid model, viscoelasticity, White-Metzner model, thixotropy

❖ INTRODUCTION

Silicone fluids (poly-dimethyl-siloxane, PDMS) have important applications in many branches of modern industry, such as automotive, electric and electronic, domestic appliances and medical [1]. Their advantages include high temperature and chemical resistance, optical transparency, and good electrical properties. Certain application areas and processing steps require a reliable rheological model. The only known previous work on the rheology of PDMS reports about PDMS samples with viscosities of 1 and 30 Pas [2]. In the present paper the silicone fluid sample AK1.000.000 is reported which is of much higher viscosity: its kinematic viscosity is approximately 1.000.000 mm^2/s at 25°C. Our aim is to create a lumped parameter model which describes the viscoelastic properties of this silicone fluid sample in shear flow [3, 4].

❖ LINEAR MODEL BASED ON TTS RULE

Rotational rheometer (Anton Paar, MCR 101) is used for our measurements. Small amplitude oscillatory shear (SAOS) curves of the silicone fluid samples in the angular frequency range of 0.628 - 628 rad/s have been measured in a broad temperature range: from 0°C to 120°C in 10°C steps.

The measured data show that the sample is thermo-rheologically simple, i.e. it obeys the time-temperature superposition (TTS) feature in this temperature range [5, 6]. Fig. 1 illustrates this with the plots of the storage and loss moduli vs. the angular frequency at temperatures of 0°C, 60°C, and 120°C, shifted to the reference temperature of 60°C. This enabled us to create a master

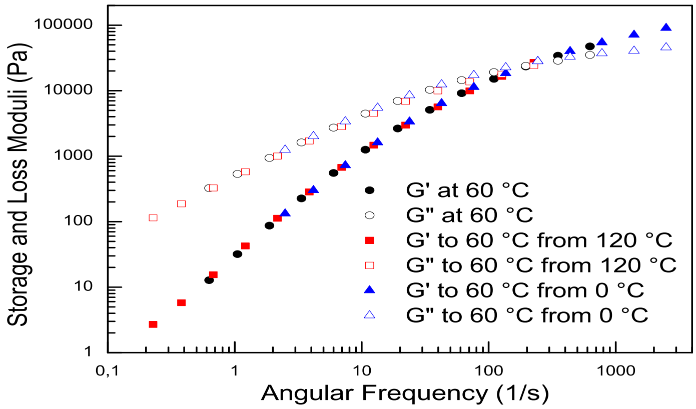

Figure 1: Time Temperature Superposition of AK1.000.000 silicone fluid. Storage (G') and loss (G") moduli, measured at 0°C, at 60°C and at 120 °C are plotted, both the 120 °C and the 0°C data are already shifted to 60°C, using the shift parameters of Fig. 2.

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curve for the reference temperature of 60°C with an increased angular frequency range of 0.2 to 2500 rad/s by using the Williams-Landell-Ferry (WLF) formula. The horizontal and vertical shift parameters are shown in Fig. 2.

A 5-element Maxwell model has been matched to the measurements for the description of the master curve with the usual method [6]. The accuracy of the model is good: the relative error of the complex viscosity is within 2.5 % in the whole frequency range. Fig. 3 shows the measured loss and storage moduli of the master curve in comparison with the computed values at 60°C.

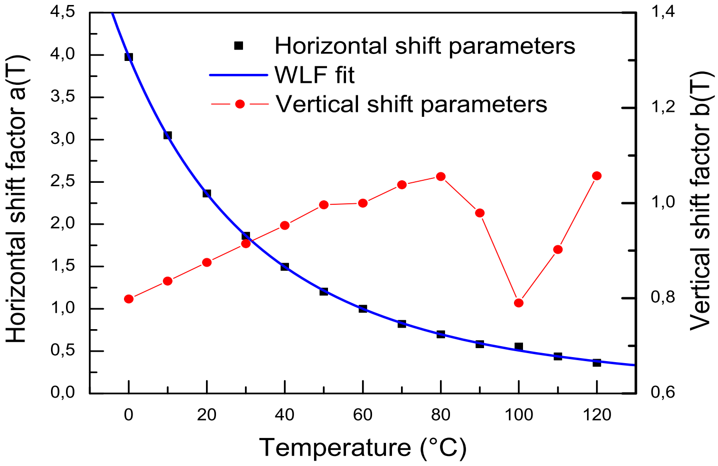

Figure 2: Horizontal (■) and vertical (●) shift parameters versus temperature are plotted. The thick blue curve represents the WLF fit (see Equation (1)) for the horizontal shift parameters with: c_0 = -6.409 and c_1 = 338.2874°C.

❖ NONLINEAR MODEL

The measurement of steady shear flow curves revealed that the sample is shear thinning and it obeys the Cox-Merz rule, i.e. the magnitude of the complex viscosity at an angular frequency equals the shear flow viscosity at that shear rate which equals the angular frequency [7]:

$$\left|\eta^*(\omega)\right| = \eta(\dot{\gamma})\Big|_{\dot{\gamma}=\omega} \qquad (1)$$

Fig. 4 shows the measured data with full symbols. Here we must note that the shear flow measurements are limited to shear rate values below 20 1/s, since at higher shear rates the sample flows out of the sample holder due to the Weissenberg effect [8].

In order to take into account the shear thinning behavior of the silicone oil, the 5-element Maxwell model is generalized in analogy of the White-Metzner model [9]. The constitutive equations are the following:

$$\tau_i(t) + \frac{\eta_i(\dot{\gamma})}{k_i}\dot{\tau}_i(t) = -\eta_i(\dot{\gamma})\cdot\dot{\gamma}(t) \qquad (2)$$

where i = 1,2,..., 5 is the mode index, and the shear rate dependent viscosity parameters are defined as

$$\eta_i(\dot{\gamma}) = \frac{\eta_i}{\sum_j \eta_j}\cdot\left|\eta^*(\omega)\right|_{\dot{\gamma}=\omega} \qquad (3)$$

In Eq. (2) and (3), the k_i and the η_i are the parameters of the 5-element linear Maxwell model, while the $\eta^*(\omega)$ is the measured complex viscosity. The accuracy of this 5-element White-Metzner model is tested by numerical simulation of the SAOS. The open symbols of Fig. 6 show that the agreement with the measured data is excellent.

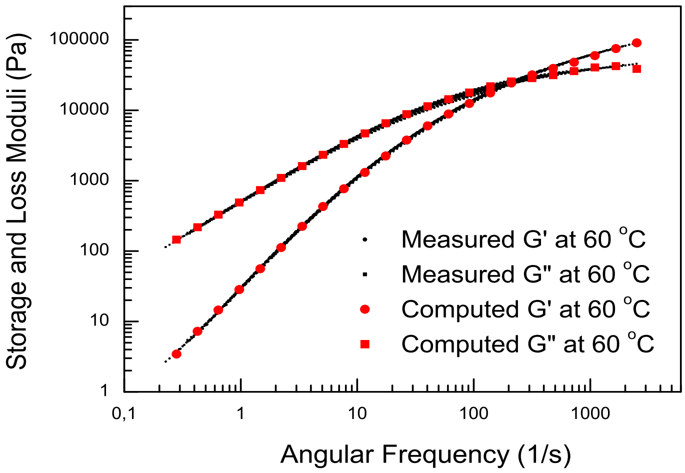

Figure 3: The master curve for 60 °C (lines), based on the measured storage and loss moduli in the temperature range of 0°C-120°C, and their computed counterparts (symbols), calculated from the 5-element linear Maxwell model

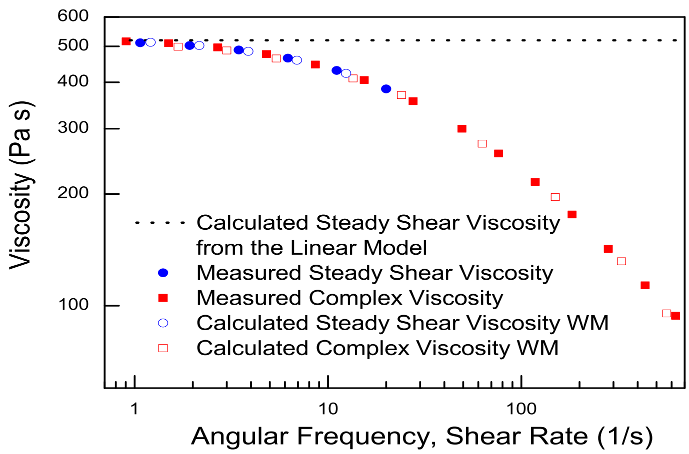

Figure 4: Measured and calculated complex viscosities vs. angular frequency, as well as measured and calculated steady shear viscosities vs. shear rate. The outstanding agreement between the measured steady shear and complex viscosities (at 60°C) means that the sample obeys the Cox-Merz rule. The data computed with the 5-element White-Metzner model are in excellent agreement with the measured values. A linear model would fail to describe the shear thinning of the sample.

❖ THIXOTROPY

The behavior of the silicone fluid has been also tested during long time steady shear flow with constant shear rate, at temperatures of 30°C and 80°C.

These tests show that there is no change in the viscosity even after an hour of shear flow at 30˚C. However, at 80˚C the viscosity decreases with time, i.e. the silicone fluid is thixotropic at this temperature. Fig. 5 shows the viscosity of the sample at 80˚C during shear flow with a shear rate of 20 1/s. The inset plots the same viscosity data vs. shear rate, in order to show the hysteresis explicitly.

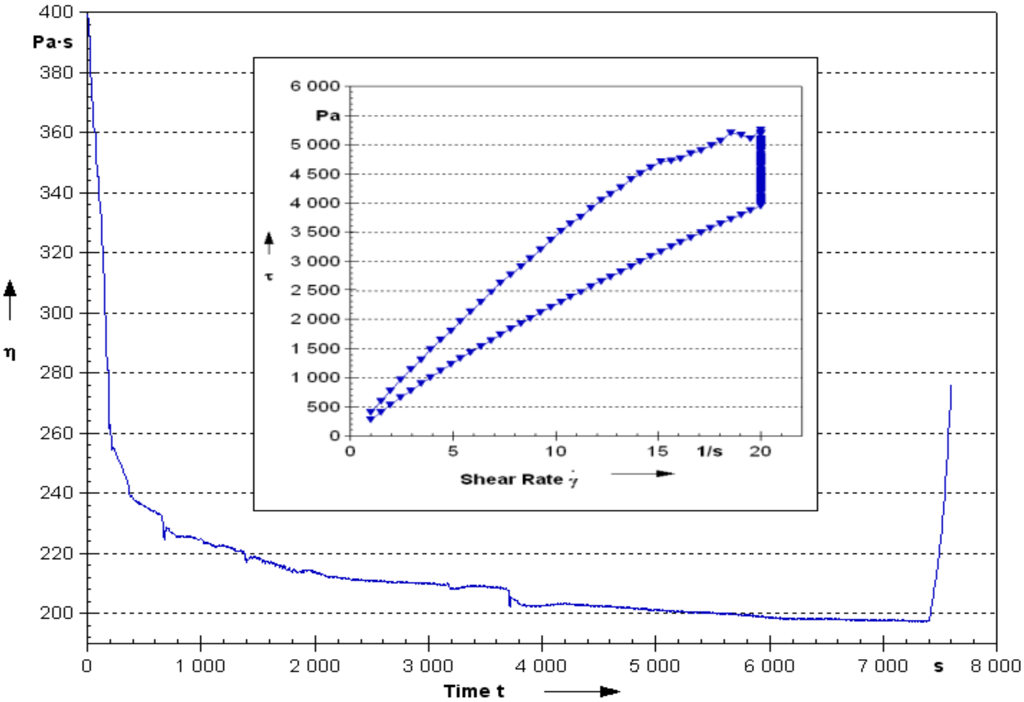

Figure 5: Viscosity of the silicone fluid at 80˚C during long time shear flow with a shear rate of 20 1/s. The inset plots the corresponding shear stress data vs. shear rate, in order to show the hysteresis more explicitly. At the start and at the end of the long time shear flow, the shear rate is ramped between 0 and 20 1/s.

Thixotropy means that the change in the material properties (caused and also maintained by the shear load) is just temporary, thus the material properties returns to their original values within a comparable time after elimination of the load. In Fig. 6 the SAOS tests of the silicone fluid are plotted in order to show how these curves after the long time shear flow of Fig. 5 approach the initial curves. The thixotropic behavior of the silicone fluid makes its rheological modeling more complex, this modeling work is presently in progress (Fig. 6).

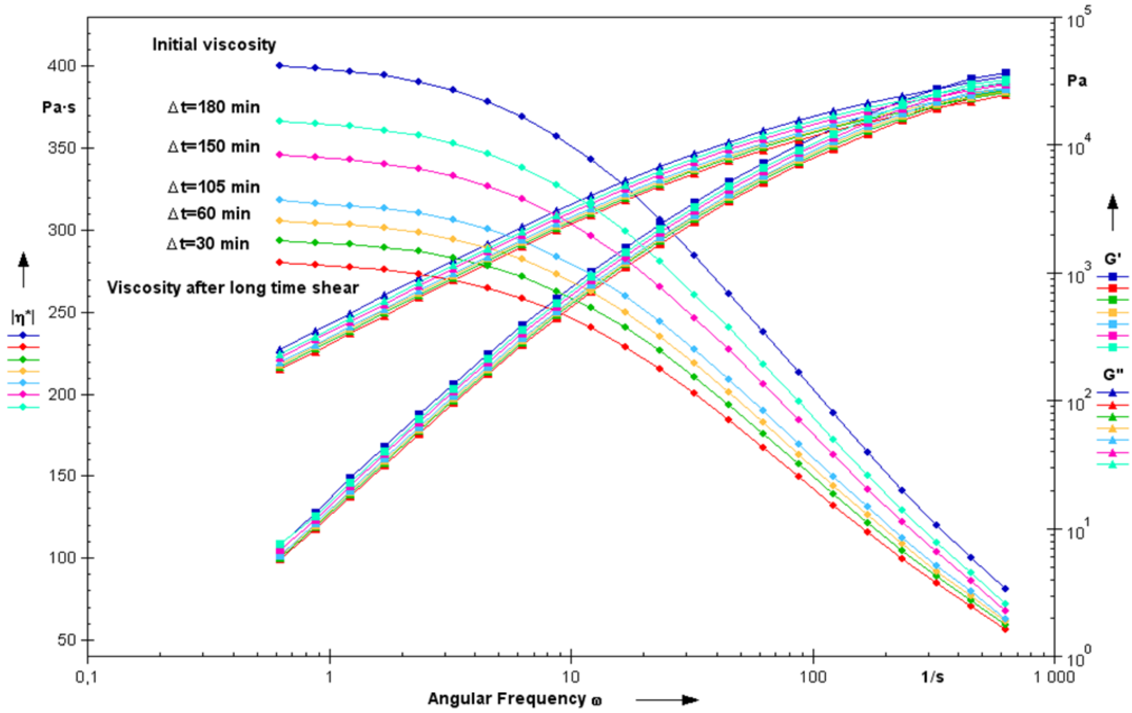

Figure 6: SAOS curves of the silicone fluid before (blue), right after (red) and with the indicated time delay (other colors) after the long time shear flow of Fig. 5. These curves show how the rheological properties of the sample approach their initial values after the long time shear flow, which means that the fluid is thixotropic.

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❖ CONCLUSION

The rheological properties of a silicone fluid (PDMS) sample are investigated in this paper with the aim of the construction of a lumped parameter model for shear flow. Based on measured SAOS and flow curves in a broad temperature range, using TTS, a 5-element Maxwell-model is defined which accurately describes the viscoelastic properties of the silicone fluid in the linear regime. A 5-mode White-Metzner model is also constructed which has built-in that the silicone fluid sample obeys the Cox-Merz rule, thus it accurately describes the nonlinear viscous properties of the sample. The silicone fluid is thixotropic in a certain temperature range, which makes its modeling more complex.

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